^{77}Se SABRE via TANDEM SCALAR COUPLING: FIRST PARAHYDROGEN-INDUCED HYPERPOLARIZATION of SELENIUM

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We demonstrate the first successful hyperpolarization of ^{77}Se nuclei using Signal Amplification By Reversible Exchange (SABRE), applied to a biologically relevant selenium–nitrogen heterocycle, 3-methyl-[1,2,4]-selenadiazolo-[4,5-a]-pyridine-4-ium chloride (SDAP)[1]. The polarization transfer was carried out at ultralow magnetic fields (0.1 μT to 5 μT), using parahydrogen as the polarization source. Remarkably, high levels of nuclear spin polarization were obtained simultaneously for both ^{77}Se and ^{15}N nuclei at their natural isotopic abundances, reaching 7.0% and 5.6%, respectively. These results enable direct detection of ^{15}N and ^{77}Se signals at micromolar concentrations, using a single scan at 9.4 T, without isotopic enrichment.

Mechanistic analysis revealed a tandem polarization transfer pathway, in which ^{77}Se polarization is relayed through scalar coupling with ^{15}N nuclei in the SABRE polarization transfer complex. This cooperative polarization mechanism enables efficient hyperpolarization of low-γ, low-abundance heteronuclei such as ^{77}Se. Our findings establish microtesla SABRE as a powerful, low-cost alternative to d-DNP for enhancing multinuclear NMR sensitivity in spin systems involving multiple heteronuclei. The demonstrated method opens new avenues for studying selenium-containing compounds in organic synthesis, catalysis, and biomedical research via heteronuclear NMR.

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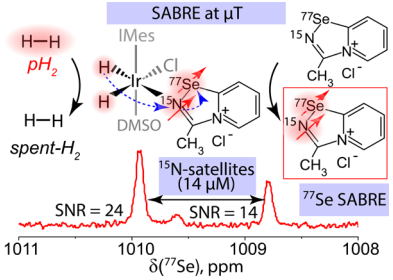

Fig. 1. Polarization of ^{77}Se nuclei via scalar interactions with parahydrogen-derived protons and ^{15}N nuclei. ^{77}Se NMR spectrum of hyperpolarized 3-methyl-[1,2,4]-selenadiazolo-[4,5-a]-pyridine-4-ium chloride (SDAP), acquired using the SABRE method at a magnetic field of 0.4 μT and room temperature. The spectrum was obtained at natural isotopic abundance of both ^{15}N and ^{77}Se. The experiment was performed in methanol-d_4 solution under 5 bar parahydrogen pressure.